THE M. W. KELLOGG COMPANY

Petroleum and Chemical Research Department

PROGRESS REPORT

ARCTIC RUBBER

U. S. Army Contract DA-44-109-qm-222
Project No. 7-93-15-604
For the Period January-March, 1953

April 1, 1953

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Petroleum and Chemical Research Department
Laboratory Division, Jersey City, New Jersey

PROGRESS REPORT

Subject: Arctic Rubber - U.S. Army Contract DA-44-109-qm-222
Project No. 7-93-15-004
For the Period January-March, 1953

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Period Covered: January 1, 1953 to March 31, 1953

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Previous Reports on this Subject:

RL-50-139	dated	November 1, 1950
RL-51-146	"	February 1, 1951
RL-51-156	"	April 1, 1951
RL-51-163	"	July 1, 1951
RL-51-174	"	October 1, 1951
RL-52-183	"	February 1, 1952
RL-52-195	"	May 1, 1952
RL-52-209	"	August 1, 1952
RL-52-248	"	October 1, 1952
RL-53-259	"	January 1, 1953

Approved:

E. F. Schwarzenbek

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I. Introduction

A. Purpose of the Project

The primary purpose of this project is the development of a fluorine containing oil- and fuel-resistant elastomer which will retain its rubbery properties between -70°F. and +160°F. A more recent objective is the pilot plant production and large scale evaluation of the more promising elastomers, with special emphasis on the polymer currently designated by M.W. Kellogg as "X-300 Rubber".

B. Research Program

To achieve this goal, the M.W. Kellogg Company has been authorized by the Quartermaster Corps to conduct a broad investigation of fluorocarbon polymers involving (1) monomer synthesis; (2) polymer preparation; and (3) polymer evaluation. Emphasis has been placed upon polymer preparation and especially upon the copolymerization of fluoroolefins and fluoro-chloro-olefins among themselves and with olefinic and diolefinic hydrocarbons.

Monomer synthesis at Kellogg has been restricted to products arising from the thermal dimerization of CF_2=CFCl, namely, CF_2=CF-CF=CF_2, CF_2-CF=CF-CF_2, and CF_3-CF=CF_2. Where feasible, the preparation of other monomers, e.g., CF_2=CF_2 and CF_2=CHF, has also been undertaken in these laboratories. For the most part, however, monomers not available commercially have been requested from Dr. Paul Tarrant of the University of Florida, Dr. Aldrich Syverson of the Ohio State University, and Dr. W.T. Miller of Cornell University, or obtained on an exchange basis from Minnesota Mining and Manufacturing Company.

Polymer preparation has proceeded through four phases: (a) exploratory copolymerization of new monomer pairs; (b) determination of the relative reactivities of monomers successfully copolymerized into elastomers; (c) synthesis of pound batches of these elastomers in several comonomer ratios for evaluation; and (d) pilot plant production of one elastomer (Kellogg "X-300 Rubber") which is of interest to the Quartermaster not so much as an Arctic Rubber but more precisely as an acid- and oxidant-resistant elastomer for protective suits, gloves, and boots. A new phase, initiated during the present quarter, will involve the testing of small samples of unvulcanized, rubbery polymers, obtained from exploratory work, for oil-resistance and low temperature flexibility. This testing program will be carried on at the Quartermaster Depot in Philadelphia.

Polymer compounding, testing, and evaluation has been carried forward most capably by Mr. C.B. Griffis and his staff at the Philadelphia Quartermaster Depot. The development of uses for X-300 has been the joint responsibility of Mr. Griffis and the Kellogg Applications Laboratory.

C. Past Progress

1. Quarters completed as of January 1, 1953: 10
2. Monomers available for copolymerization: 38

   a. Purchased: 17
   b. Minnesota Mining & Mfg. Company: 3
   c. Dr. Tarrant: 8
   d. Dr. Syverson: 4
   e. M.W. Kellogg Company: 6

3. Copolymer systems investigated: 142
   (where the numbers refer to the monomers listed in section III-A below):

   1-2, 1-2-4, 1-2-9, 1-2-14, 1-2-21, 1-2-22, 1-2-24, 1-2-29, 1-2-30, 1-2-32, 1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 1-9, 1-12, 1-13, 1-14, 1-16, 1-17, 1-18, 1-19, 1-20, 1-21, 1-22, 1-23, 1-25, 1-27, 1-28, 1-30, 2-3, 2-4, 2-6, 2-8, 2-9, 2-12, 2-13, 2-15, 2-16, 2-17, 2-18, 2-19, 2-21, 2-22, 2-23, 2-24, 2-28, 2-29, 2-30, 2-32, 2-34, 2-38, 3-4, 3-7, 3-9, 3-14, 3-18, 3-19, 3-20, 3-21, 3-22, 3-23, 3-24, 3-25, 3-30, 3-32, 4, 4-5, 4-6, 4-8, 4-9, 4-10, 4-11, 4-12, 4-14, 4-15, 4-17, 4-19, 4-20, 4-21, 4-22, 4-24, 4-25, 4-27, 4-28, 4-29, 4-32, 5-9, 6-8, 6-9, 6-30, 8-13, 8-24, 9, 9-12, 9-13, 9-14, 9-16, 9-17, 9-18, 9-22, 9-23, 9-27, 9-28, 10-14, 10-28, 12-24, 13-17, 13-18, 14-22, 14-28, 16-18, 16-24, 17-18, 17-24, 18-21, 19-22, 19-28, 20-22, 20-28, 21, 21-22, 21-28, 21-30, 22, 22-24, 22-28, 22-32, 22-38, 23-28, 24-28, 24-31, 25-28, 27, 27-28, 28, 28-30, 28-32, 30, and 37.

4. Rubberlike systems: 62

   1-2, 1-2-14, 1-2-21, 1-2-22, 1-2-24, 1-2-29, 1-2-30, 1-2-32, 1-3, 1-5, 1-13, 1-17, 1-22, 1-28, 2-4, 2-6, 2-13, 2-17, 2-22, 2-24, 2-28, 2-30, 2-32, 2-34, 3-4, 3-9, 3-14, 3-18, 3-19, 3-21, 3-22, 3-23, 3-24, 3-32, 4-5, 4-28, 5-9, 9-12, 9-13, 9-17, 9-28, 12-28, 13-18, 14-22, 14-28, 17-18, 17-24, 20-22, 21, 21-22, 21-28, 22, 22-24, 22-28, 22-32, 24-28, 24-31, 27-28, 28, 28-30, 28-32, and 37.

5. Monomer reactivity ratios determined: 8

M_1	M_2	r_1	r_2
$CF_2=CF_2$	Butadiene	0.0	1.75
$CF_2=CFCl$	"	0.0	1.35
$CF_2=CCl_2$	"	0.0	0.80
$CF_2=CF-CF=CF_2$	"	0.0	1.35
$CF_2=CFCl$	Isoprene	0.1	1.41
$CF_2=CCl_2$	"	0.0	0.45
$CF_2=CF-CF=CF_2$	"	0.0	0.75
$CF_2=CFCl$	$CF_2=CH_2$	0.52	0.17

6. Status of rubberlike systems:

   a. Most promising in pilot plant and undergoing extensive tests: 1-2.
   b. Evaluated and rejected as unpromising: 1-3, 1-5, 1-17, 3-9, 5-9, 21, 22, and 28.
   c. Promising, should be evaluated further: 1-2-14, 1-2-21, 1-2-22, 1-2-24, 1-2-29, 1-13, 1-22, 1-28, 2-22, 2-24, 2-30, 2-32, 2-34, 3-4, 3-24, 4-28, 9-13, 9-28, 12-28, 17-24, 21-22, 22-24, 24-28, 24-31 and 28-32.

   d. Interesting, but better recipes needed to increase yields or to increase proportion of fluorocarbon combined: 2-4, 2-28, 3-14, 3-18, 3-19, 3-21, 3-23, 14-22, 14-28, 21-28, 22-32, 27-28, 28-30, and 37.

   e. Relatively uninteresting because of very low fluorine content or obviously unsatisfactory physical appearance: 2-6, 2-13, 2-17, 3-22, 4-5 (isoprene copolymers no longer of interest), 9-12, 9-17, 13-18, 17-18, and 20-22.

7. Alfin and anionic (Na) polymerizations of fluoro-olefins unsuccessful.

8. No glass transition temperature noted for Teflon, "KEL-F", polyperfluorobutadiene, or polytrifluoroethylene from -150°C. to 85°C.

9. Vulcanization of "unsaturated" rubbers partially successful with Na_2S_x and peroxide-amine recipes.

10. Vulcanization of $CF_2=CFCl/CH_2=CF_2$ copolymer (X-300) successful with diisocyanates, apparently catalyzed by zinc oxide.

11. Physical properties of $CF_2=CFCl/CF_2=CH_2$ copolymer (X-300), vulcanized by diisocyanates, determined at several ratios of combined monomers.

II. Summary of Current Progress

The number of monomers available for copolymerization studies has increased to 44, the number of copolymer systems investigated to 239, and the number of rubberlike systems to 92.

Five additional vulcanizing agents, making a combined total of seven have been sent to the QM Depot for evaluation as curatives for X-300. Results from evaluations of three of these have been received and one, curing agent 180-56, appears promising.

A five pound sample of 30/70 and a fifteen pound sample of 42/58 molar CF_2=CFCl/CF_2=CH_2 copolymer have been shipped to the Depot for more complete evaluation of these levels. A one-half pound sample of an approximately 43/53/4 molar CF_2=CFCl/CF_2=CH_2/CF_3-CF=CF_2 terpolymer has also been submitted for test.

Recipes and operating procedures for the X-300 pre-pilot plant have received extensive study and progress has been made toward establishing better control of the polymerization.

During this quarter, 272 pounds of X-300, made in the pre-pilot plant, have been shipped to QM.

A rapid method for comparing the low-temperature and oil-resistance properties of small samples of raw, rubbery polymers has been devised. These tests should speed our selection of a few of the exploratory materials for more extensive compounding, curing, and evaluation studies.

III. Experimental Section

A. Monomer Synthesis

Forty-four monomers are now available for copolymerization studies:

1. $CF_2=CFCl$
2. $CF_2=CH_2$
3. $CH_2=CH-CH=CH_2$
4. $CF_2=CF-CF=CF_2$
5. $CH_2=C(CH_3)-CH=CH_2$
6. $(CH_3)_2C=CH_2$
7. $\overline{CF_2-CF=CF-CF_2}$ (ring)
8. $CH_2=CHCl$
9. $CF_2=CCl_2$
10. $CH_3-CH=CH_2$
11. $C_6H_5-CH=CH_2$
12. $CH_2=CCl_2$
13. $CH_2=CCl-CH=CH_2$
14. $CF_3-CF=CF_2$
15. $CF_2=CF-CN$
16. $CH_2=CH-CN$
17. $CH_2=CH-CO_2-C_4H_9$ (n)
18. $CF_2=CHCl$
19. $CF_3-CCl=CCl-CF_3$
20. $CF_3-C\equiv C-CF_3$
21. $CF_2=CFH$
22. $CH_2=CFCl$
23. <u>cis</u> $CF_3-CH=CH-CF_3$
24. $CF_2=CF_2$
25. <u>trans</u> $CF_3-CH=CH-CF_3$
26. $CH_2=CH-C_6H_4-CH=CH_2$
27. $CH_2=C{<}^{CF_3}_{CH_3}$
28. $CH_2=CF-CH=CH_2$
29. $CF_2=C{<}^{CF_3}_{CF_3}$
30. $CF_2=CFBr$
31. $CH_2=CH_2$
32. $CF_2=CCl-CF_3$
33. $CF_3-C(CH_3)=CH-COOH$
34. $CH_2=CH-C(=O)-NH_2$
35. $CF_3-CH=CH_2$
36. $CH_2=CHBr$
37. $CF_2=CH-CH=CH_2$
38. $CF_3-CCl=CCl_2$
39. $CF_3-CCl=CH_2$
40. $CH_2=CHF$
41. $CF_2=CH-C(CH_3)=CH_2$
42. $CF_3-CH=CF_2$
43. $CF_3-CH=CH-CH=CH_2$
44. $CF_2=C(CH_3)-CH=CH_2$

Dr. Tarrant of the University of Florida has prepared two of the new monomers:

#41 $CF_2{=}CH{-}C(CH_3){=}CH_2$ 237 g., b.p. 35/35.5°C.

Preparation:

$$CF_2Br_2 + CH_2{=}C(CH_3)_2 \xrightarrow[\text{peroxide}]{\text{benzoyl}} CF_2Br{-}CH_2{-}CBr(CH_3)_2$$

$$\xrightarrow[\text{t-amines}]{-2HBr} CF_2{=}CH{-}C(CH_3){=}CH_2$$

#42 $CF_2{=}C(CH_3){-}CH{=}CH_2$ 114 g., b.p. 37/38.5°C.

Preparation:

$$CF_2Br_2 + CH_3{-}CH{=}CH{-}CH_3 \xrightarrow[\text{peroxide}]{\text{benzoyl}} BrCF_2{-}CH(CH_3){-}CHBr{-}CH_3$$

$$\xrightarrow[\text{t-amines}]{-2HBr} CF_2{=}C(CH_3){-}CH{=}CH_2$$

Dr. Syverson of the Ohio State University has submitted three of the new monomers:

#39 $CF_3{-}CCl{=}CH_2$ 104 g., b.p. 12-13.5°C.

#42 $CF_3{-}CH{=}CF_2$ 298 g., b.p. -17 to -15°C.

#43 $CF_3{-}CH{=}CH{-}CH{=}CH_2$ 57 g., b.p. 44-45.5°C.

Preparation of #43:

$$CF_3{-}CO_2Et + CH_3C({=}O){-}CH_3 \xrightarrow{\text{NaOEt}} CF_3{-}C({=}O){-}CH_2{-}C({=}O){-}CH_3$$

$$\xrightarrow{H_2} CF_3{-}CH(OH){-}CH_2{-}CH(OH){-}CH_3 \xrightarrow[\text{anhydride}]{\text{acetic}} CF_3{-}CH(OAc){-}CH_2{-}CH(OAc){-}CH_3$$

$$\xrightarrow{\text{pyrolysis}} CF_3{-}CH{=}CH{-}CH{=}CH_2$$

The sixth new monomer was a complimentary sample from General Chemical Division, 1000 gm. of $CH_2=CHF$ (#40).

A 300 g. sample of $CF_2=CF-CF=CF_2$ was shipped to Minnesota Mining and Manufacturing Company in exchange for an equal quantity of $(CF_3)_2C=CF_2$.

Dr. Syverson has been requested to make substantial quantities of $CF_2=CFH$ and $CF_2=CFBr$.

Monomers for Infra-Red Study

The following monomers were shipped to Dr. Peter King of the High Polymer Section, Naval Research Laboratory, Washington 25, D.C. for the determination of infra-red spectra: $CF_2=CF-CF=CF_2$, $CF_2=CHCl$, $CF_3-C{\equiv}C-CF_3$, $CF_2=CHF$.

Compounds for Vibrational Spectrum Measurements

Fifty gram samples of $CF_2=CFBr$, $CF_2Br-CFHCl$ and $CF_2Br-CHCl_2$ and a 200 g. sample of $CFCl_3$ were sent to Dr. D.E. Mann in the Thermodynamics Section of the National Bureau of Standards for determination of vibrational spectra.

B. Monomer Analysis

The following monomers have been analyzed with the mass spectrometer:

1. $CF_2=CHCH=CH_2$ — Tank No. 858M-37-2

$CF_2=CHCH=CH_2$	91%
$CF_3-CH=CH-CF_3$ (probable)	6-8%

2. $CF_2=CHC(CH_3)=CH_2$ — Tank No. 858M-41-1

$CF_2=CHC(CH_3)=CH_2$	99.7%
HF addition product	0.2%
Compound of molecular wt. 129-131	0.1%

Presence of low molecular weight impurities cannot be established definitely.

3. $\underline{CF_2=CFCF=CF_2}$ — Tank No. 858M-4-1

$CF_2=CFCF=CF_2$	93%
Air	3.5%
C_4HF_5	0.5%
$C_4H_2F_4$	1.5%
$C_4H_3F_3$	0.4%

4. $\underline{CF_2=CFCF=CF_2}$ — Tank No. 858M-4-2

$CF_2=CFCF=CF_2$	99%
$CF_2HCF=CF-CF_2H$ (possible)	0.3%
C_4F_5H	0.3%

5. $\underline{CF_2=CFCF=CF_2}$ — Tank No. 858M-4-3

$CF_2=CFCF=CF_2$	97%
$C_4F_4H_2$	1-2%
C_4F_5H	1%
$C_4H_3F_3$	0.3%

The FBD in Tank No. 858M-4-1 is a combination of the fore-runs of a number of distillations, b.p. 5-6.2°C. Tank 858M-4-2 is a combination of a number of heart cuts, b.p. 6.2-6.3°C. Tank 858M-4-3 is a heart cut from a distillation containing bottoms from a previous distillation.

6. $\underline{CF_2=CF-CF=CF_2}$ — Tank No. D-122M-4-4

$CF_2=CF-CF=CF_2$	96%
C_4F_5H	1%
$C_4F_4H_2$ (apparently)	1%
$C_4H_3F_3$	trace
Cl compound or compounds	from <1% to 2%

7. $\underline{CF_2=CF-CF=CF_2}$ — Tank No. D-122M-4-5

$CF_2=CF-CF=CF_2$	93-94%
C_4F_5H	4+%
$C_4F_6H_2$	0.6%
$C_4F_5H_3$	0.3%
$C_4F_3H_3$	0.1%
dichloro compounds	0.1 + %
C_5 compounds	0.1%
Air	0.6%

8. $CF_2=CF-CF=CF_2$ Tank No. D-122M-4-6

C_4F_6	97.2%
C_4F_5H	2.2%
$C_4F_4H_2$	0.4%
$C_4F_3H_3$	0.1%
C_5 compounds	0.05%
possible trace (<0.05%) of $C_4F_6H_2$	

Tank No. D-122M-4-4 and Tank No. D-122M-4-6 are heart cuts, b.p. 6.2-6.3°C. Tank No. D-122M-4-5 is a combination of tails from a number of distillations. Tank No. D-122M-4-6 made up most of the 300 g. of $CF_2=CF-CF=CF_2$ shipped to Minnesota Mining & Mfg. Co. in exchange for an equal quantity of $(CF_3)_2C=CF_2$ already received.

9. cis-$CF_3-CH=CH-CF_3$ Tank No. D-122M-23-1

C_4F_6H	97.5%
C_4F_6HCl	~0.5%
3-H to 5-H compounds, showing C_2H_3- and C_2H_5- groups	~2%

10. trans-$CF_3-CH=CH-CF_3$ Tank No. D-122M-25-1

C_4F_6H	92.5%
C_4F_6HCl	~4.5%
3-H to 5-H compounds, showing C_2H_3 and C_2H_5 groups	~3.0%

11. $CF_3-CCl=CH_2$ Tank No. D-122M-39-1

$CF_3-CCl=CH_2$ (& possibly isomers thereof)	>97%
N_2	~1%
C_2H_3- and C_2H_5 containing compounds	<3%

12. $CH_2=CHF$ Tank No. D-122M-40-1

$CH_2=CHF$	~99.4%
N_2	~0.3%
$CH_2=CF_2$	0.1%
CH_2F_2 (?)	0.3%

13. CF_2-CF=CF-CF_2 — Tank No. D-122M-7-1

C_4F_6	100.0%
$C_4F_5H_2$	minute traces possible
C_4F_5H	"
C_2H_5	"

14. CF_2=CF-CN — Tank No. D-122M-15-1

CF_2=CF-CN	99.7%
C_2H_2FCl	0.3%

15. CF_2=CF-CN — Tank No. D-122M-15-2

CF_2=CF-CN	99.5%

Traces of impurities. Appears to contain:

HCN	0.2%
$C_2F_2(CN)_2$	0.1%
C_2 compounds	0.2%
dihydrogen compounds	0.1%

16. CF_3-C≡C-CF_3 — Tank No. D-122M-20-1

CF_3-C≡C-CF_3	92.2%
$C_4F_6Cl_2$	0.3%
C_4F_6HCl	3.0%
$C_4F_6H_2$	4.5%

17. CH_2=CFCl — Tank No. D-122M-22-1 (Redistilled; see M.W. Kellogg Progress Report for period October-December, 1953 - RL-53-259, p. 9, for original analysis showing 1.6 mole % propene.)

Fraction II

CH_2=CFCl	98.2%
CH_3-CH=CH_2	0.2%
C_2H_3Cl (possibly)	~1.5

Fraction III

CH_2=CFCl	99.9%
CH_3-CH=CH_2	0.05%
benzene or C_3 fluorocarbon	0.1 - 0.2%

18. CF_3-CH=CF_2 Tank No. D-122M-42-1

C_3F_5H	99.6%
N_2	0.4%

C. Polymer Preparation

Copolymerizations have now been attempted with 239 systems (where the numbers refer to monomers listed in section III-A above): 1-2, 1-2-4, 1-2-9, 1-2-11, 1-2-14, 1-2-21, 1-2-22, 1-2-23, 1-2-24, 1-2-29, 1-2-30, 1-2-31, 1-2-32, 1-2-35, 1-2-40, 1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 1-9, 1-12, 1-13, 1-14, 1-16, 1-17, 1-18, 1-19, 1-20, 1-21, 1-22, 1-23, 1-25, 1-27, 1-28, 1-30, 1-35, 1-36, 1-37, 1-39, 1-41, 2-3, 2-4, 2-6, 2-8, 2-9, 2-12, 2-13, 2-15, 2-16, 2-17, 2-18, 2-19, 2-21, 2-22, 2-23, 2-24, 2-28, 2-29, 2-30, 2-32, 2-34, 2-35, 2-37, 2-38, 2-39, 3-4, 3-7, 3-9, 3-14, 3-18, 3-19, 3-20, 3-21, 3-22, 3-23, 3-24, 3-25, 3-30, 3-32, 4, 4-5, 4-6, 4-8, 4-9, 4-10, 4-11, 4-12, 4-14, 4-15, 4-17, 4-19, 4-20, 4-21, 4-22, 4-24, 4-25, 4-27, 4-28, 4-29, 4-32, 4-35, 4-37, 4-39, 4-41, 5-9, 6-8, 6-9, 6-30, 6-37, 6-41, 7-35, 7-37, 7-41, 8-13, 8-24, 8-35, 8-37, 8-41, 9, 9-12, 9-13, 9-14, 9-16, 9-17, 9-18, 9-22, 9-23, 9-27, 9-28, 9-35, 9-36, 9-37, 9-39, 9-41, 10-14, 10-28, 11-41, 12-24, 12-35, 12-37, 12-41, 13-17, 13-18, 14-22, 14-28, 14-35, 14-37, 14-41, 16-18, 16-24, 16-35, 16-37, 16-41, 17-18, 17-24, 17-35, 17-37, 17-41, 18-21, 19-22, 19-28, 19-35, 20-22, 20-28, 20-35, 20-37, 20-41, 21, 21-22, 21-28, 21-30, 21-35, 21-37, 21-41, 22, 22-24, 22-28, 22-30, 22-32, 22-35, 22-36, 22-37, 22-38, 22-41, 23-28, 23-35, 23-37, 23-41, 24-28, 24-31, 24-35, 24-36, 24-37, 24-39, 24-41, 25-28, 25-35, 25-37, 25-41, 27, 27-28, 27-37, 27-38, 27-41, 27-35, 28, 28-30, 28-32, 29-35, 29-37, 30, 30-35, 30-37, 30-41, 31-35, 32-35, 32-37, 32-41, 33-35, 33-37, 33-41, 34-37, 34-41, 35, 35-36, 35-37, 35-41, 37, 37-38, 37-39, 37-40, 38-41, 39, 39-41, 41, and 41-42.

Ninety-two of these systems can be considered rubberlike: 1-2, 1-2-14, 1-2-21, 1-22-22, 1-2-23, 1-2-24, 1-2-29, 1-2-30, 1-2-31, 1-2-32, 1-2-34, 1-3, 1-5, 1-13, 1-17, 1-22, 1-28, 1-37, 1-41, 2-4, 2-6, 2-13, 2-17, 2-22, 2-24, 2-28, 2-30, 2-32, 2-34, 3-4, 3-9, 3-14, 3-18, 3-19, 3-21, 3-22, 3-23, 3-24, 3-32, 4-5, 4-28, 4-37, 4-41, 5-9, 6-41, 7-41, 8-37, 8-41, 9-12, 9-13, 9-17, 9-28, 9-37, 9-41, 12-28, 12-37, 12-41, 13-18, 14-22, 14-28, 16-41, 17-18, 17-24, 17-35, 17-41, 20-22, 21, 21-22, 21-28, 21-37, 21-41, 22, 22-24, 22-28, 22-32, 22-41, 24-28, 24-31, 24-41, 27-28, 27-37, 27-41, 28, 28-30, 28-32, 28-35, 30-37, 31-35, 37, 37-39, 37-41, 39-41, and 41.

Recent experimental data relative to many of these systems are set forth below:

1. CF_2=CH-CH=CH_2 Copolymers

An additional supply of this monomer was received recently and a large number of copolymerizations have been carried out with other monomers listed in Section III-A, (cf. Table I). The analysis of the sample of CF_2=CH-CH=CH_2 indicates it is only 91% pure (see Section III-B, Tank 858M-37-2).

In contrast to butadiene itself, 1,1-difluorobutadiene yields a homopolymer which is not rubbery at room temperature (run 1018, mutual recipe at 50°C, Table I). An earlier sample of this homopolymer, obtained from the polymerization of the monomer on storage (see M. W. Kellogg Progress Report for October-December, 1952, RL-52-259, p. 14), appeared to have some small amount of rubbery character. Certain copolymers of this diene, however, show definite rubberlike behavior. While the $CF_2=CF_2$ and $CF_2=CFH$ copolymers (runs 1129 and 1016, Table I) are hard and inelastic, the $CF_2=CFCl$ and especially the $CF_2=CCl_2$ copolymers are rubbery (runs 1012 and 1015, Table I). From these results it appears that it is the chlorine atom which brings out the latent rubberiness in these 1,1-difluorobutadiene copolymers.

An interesting result from the exploratory work with this diene is the unexpectedly large amounts of comonomers such as $CF_3-CH=CH_2$, $CF_3-C(CH_3)=CH_2$, and $CF_3-CCl=CH_2$ which copolymerize (runs 1040, 1044 and 1090). Further investigation of these systems is contemplated to determine how real these preliminary results are.

2. $CF_2=CH-C(CH_3)=CH_2$ Copolymers

This diene forms a rubbery homopolymer, and many of its copolymers are remarkably rubbery. These rubbers are in general tough, a little slow, and have the property of being capable of being stretched out into thin, transparent films which have good resistance to tear.

Both $CF_2=CH-CH=CH_2$ and $CF_2=CH-C(CH_3)=CH_2$ behave in copolymerization much like reactive dienes, such as butadiene and isoprene, rather than like the relatively unreactive perfluorobutadiene.

Copolymers of $CF_2=CH-C(CH_3)=CH_2$ are described in Table II. The analysis of the sample of this diene used appears in Section III-B, 2.

3. $CF_3-CH=CH_2$ and $CF_3-CCl=CH_2$ Copolymers

Both these monomers failed to homopolymerize and copolymerized only poorly with other halogenated olefins (Table III). However, with reactive, conjugated monomers such as the two dienes just described, it was found that varying amounts of these halopropenes could be combined. At present it is thought that these two propenes do not hold much promise. The analysis of the $CF_3-CH=CH_2$ sample used appears in the M. W. Kellogg Progress Report for October-December, 1952 RL-52-259, p. 12. Analysis of the $CF_3-CCl=CH_2$ sample is included in this report, Section III-B, 11.

4. CF_2=CFCl/CF_2=CH_2/X Terpolymers

One-half pound of the terpolymer where X is CF_3-CF=CF_2 was prepared and sent to the Depot for evaluation. Runs 848, 956 and 964-969 made up this sample (Table IV). This composite sample was blended by milling and an analysis of the blend showed a ratio of CF_2=CFCl/CF_2=CH_2/CF_3-CF=CF of 43/53/4 molar.

Several additional terpolymerization experiments have been carried out and these are also listed in Table IV. The terpolymer where X is CF_2=CFH is rubbery, as is the terpolymer where X is CH_2=CFCl. Both terpolymers have been held to low conversion (runs 1190, 909; Table IV) and analyses indicate appreciable amounts of all three monomers in each. The CF_2=CFBr terpolymer is rubbery but rather stiff and hard (run 955). Products obtained where X is CH_2=CH_2 and CH_2=CFH (987, 976 and 1088) apparently contain some of the third monomer, since the products are noticeably less rubbery than X-300 (50/50 molar CF_2=CFCl/CF_2=CH_2). However, the analyses do not indicate that much of the third monomer is combined in either case.

5. Miscellaneous Exploratory Copolymerizations

A number of miscellaneous copolymerizations are shown in Table V. Only one of these (808), a 92/8 copolymer of CH_2=CFCl/CF_3-CF=CF_2, is rubbery.

D. Polymer Evaluation

1. Screening of Raw Polymers

Up to the present time a one-pound sample of each copolymer has been required in order to test it as an Arctic Rubber. The copolymer is vulcanized and then subjected to conventional rubber tests.

The preparation of such a large copolymer sample has in practice entailed the expenditure of much time and often prohibitive amounts of rare monomers before a reasonably homogeneous sample could be obtained. Consequently, only a relatively small number of the rubbery systems prepared have been evaluated to date.

It was decided, therefore, after consultation with Mr. Griffis of the QM Depot, to attempt to screen all rubbery products as raw polymers by measuring the Gehman stiffness and volume swell in ASTM reference fuel No. 2 (60% diisobutylene, 20% toluene, 15% xylene and 5% benzene). For such screening only a few grams of each sample will be required. The sample will be molded at a suitable temperature in a mold measuring 1" x 2" x 0.070".

While the results of such a screening test cannot serve in place of a complete evaluation of the cured rubber, it is believed that the proposed screening represents the best available means of sorting out the more interesting systems from the growing list of rubbery copolymers prepared (92 up to April 1, 1953).

Accordingly, the rubbery copolymers in Table VI have been submitted to the Depot for the screening test.

2. Evaluation of $CF_2{=}CFCl/CF_2{=}CH_2$ Copolymer (M. W. Kellogg Co. X-300 Rubber)

a. Vulcanization

Up to the present time, seven potential curing agents have been synthesized at M.W. Kellogg Company and shipped to the QM Depot for evaluation. Five of these were shipped during the past quarter: 105-52, 105-56, 180-100, 180-104, and 180-108.

Results from a study of the curing of X-300 with M.W. Kellogg curing agents 105-35, 180-56 and 105-52 are shown in Table VII. The most promising of the three curatives is 180-56; five pounds will be shipped to the QM in the near future.

b. Softeners and Fillers

An extensive softener and filler study is underway at the QM Depot but the data are still too sketchy to report here.

c. Improved X-300

In an attempt to improve the low temperature properties of X-300 rubber, experimental samples of 30/70 and 42/58 molar $CF_2{=}CFCl/CF_2{=}CH_2$ copolymers were prepared and shipped to the QM Depot for comparison with the standard 50/50 product.

d. QM End Items Fabricated from X-300 Rubber

A six inch groove-type gasket was fabricated at the Depot for the Corps of Engineers, Fort Belvoir, Virginia. After eight hours immersion in RFNA the gasket was apparently unaffected. Field tests are scheduled.

Fifteen yards of X-300 coated cotton have been made at Hodgman Rubber Company and two pairs of unsupported X-300 gloves made at the Philadelphia Depot for WFNA and gas permeability tests by the Chemical Corps. If these tests are successful, a number of suits will be made up for field tests. Boots, however, await the development of a softer, more easily calendered X-300 stock.

e. Mooney Viscosity Tests

Approximately three pounds of X-300 were sheeted out and half the batch compounded with MDI-ZnO and again sheeted for Mooney viscosity measurements at Scott Testers, Providence, R.I. With the large Mooney rotor at 212°F., a surge value of more than 200 points (off-scale) was observed for the raw polymer. However, with the small rotor at 250°F. the surge value was brought on scale and a constant value of 39 points observed for the raw gum. The compounded stock has a Mooney value of 43 points under the same conditions. The Mooney viscometer should be a useful means of controlling the quality of X-300 made in the pilot plant and of measuring the plasticity of compounded stocks. An instrument has been ordered for delivery in 30-90 days.

f. Analytical Studies

An infrared method has been developed for determining rapidly the composition of pressed sheets of CF_2=CFCl/CF_2=CH_2 copolymers to replace time consuming gravimetric chloride and fluoride analyses.

E. Pilot Plant Production of X-300 Rubber

1. Pilot Plant Operation

During the past quarter operating procedure has been further modified to bring the conversion to a satisfactory level (50%) and the polymer composition more consistently within the currently specified limits of 45-53 mole % CF_2=CFCl.

2. Cumulative total of X-300 shipped to QM Depot

Month	Weight, lb.
January	59.0
February	81.1
March	131.8
	271.9 lb.

IV. Plans for Future Work

1. Pilot Plant production of X-300 for thorough evaluation in a variety of end items (of immediate interest: protective suits, hoods, gloves, and boots).

2. Filler and Softener studies on X-300.

3. Improved X-300 polymer (better low temperature properties).

4. Screening the more promising rubbers noted in the "Past Progress" section by means of Gehman stiffness and volume swell measurements on pressed sheets of the raw polymers.

5. Exploratory polymerization of new monomer pairs and development of better recipes where needed to improve yields.

References to Original Records

Notebook #135	(A.N. Bolstad)	pp. 174-188
Notebook #168	(J.M. Hoyt)	pp. 143-200
Notebook #226	(J.M. Hoyt)	pp. 1-4
Notebook #202	(F.N. Roberts)	pp. 48-159
Notebook #196	(W.M. Sims)	pp. 62-136
Notebook #219	(W.M. Sims)	pp. 14-32

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J. M. Hoyt
J. M. HOYT

J. W. Copenhaver
J. W. COPENHAVER

TABLE I

COPOLYMERS OF $CF_2=CH-CH=CH_2$

Recipe: Mutual, 22-24 hours, 50°C.
Molar Ratio Charged: 50/50

Run No.	Comonomer	% Conversion	Moles $CF_2=CH-CH=CH_2/X$ Combined	Appearance
1036	$(CH_3)_2C=CH_2$	30	99/1	soft, slow rubber
1037	$CF_2-CF=CF-CF_2$	29	96/4	hard rubber
1038	$CF_3-CF=CF_2$	27	92/8	hard rubber
1039	$CH_2=CHCl$	27	79/21	soft, slow rubber
1040	$CF_3-CH=CH_2$	30	76/24	medium rubber
1044	$CF_3-C(CH_3)=CH_2$	37	78/22	soft rubber
1045	$CH_2=CCl_2$	6	72/28	soft, sticky rubber
1046	$CF_2=CFBr$	11	92/8	medium rubber
1048	$CF_3C\equiv C-CF_3$	14	96/4	powder
1049	$CF_2=CH-C(CH_3)=CH_2$	92 /1/	80/20	soft rubber
1051	$CH_2=CH-CN$	40	52/48	tough, yellow solid
1089	$CH_2=CH-CO_2-C_4H_9$ (n)	68	98/2	tough, snappy rubber
1090	$CF_3-CCl=CH_2$	42	84/16	soft rubber
1123	$CH_3C(CF_3)=CH-COOH$	8	82/18	soft solid
1124	$CF_3-CCl=CF_2$	35	98/2	flaky powder
1122	$(CF_3)_2C=CF_2$	9	88/12	pink powder
1125	$CH_2=CH-CO-NH_2$	100	47/53	glassy, brittle solid
1127	$CF_3-CCl=CCl_2$	32	99/1	powder
1041	$CH_2=CFCl$	32	93/7	crumbly solid
1042	cis $CF_3-CH=CH-CF_3$	32	94/6	white solid
1043	trans $CF_3-CH=CH-CF_3$	32	89/11	powder

TABLE I
(Continued)

Run No.	Comonomer	% Conversion	Moles CF_2=CH-CH=CH_2/X Combined	Appearance
1012	CF_2=CFCl	38	85/15	short, weak rubber
1013	CF_2=CF-CF=CF_2	43	68/32	stiff, short rubber
1015	CF_2=CCl_2	43	84/16	tough, very elastic rubber
1016	CF_2=CFH	45	62/38	hard, crumbly solid
1017	CH_2=CCl_2	43	66/34	soft, sl. rubbery gum
1018	none	85	--	powder

Recipe: Cumene Hydroperoxide Redox, 24 hrs., 20°C.
Molar Ratio Charged: 50/50

Run No.	Comonomer	% Conversion	Moles CF_2=CH-CH=CH_2/X Combined	Appearance
1129	CF_2=CF_2	37	85/15	very short, hard rubber
1131	CF_2=CH_2	33	68/32	hard, crumbly solid

Recipe: Persulfate-bisulfite-iron suspension, 21 hrs., 20°C.
Molar Ratio Charged: 50/50

Run No.	Comonomer	% Conversion	Moles CF_2=CH-CH=CH_2/X Combined	Appearance
1136	CH_2=CHF	13	--	white powder

/1/ Analytical results unexplained.

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TABLE II

COPOLYMERS OF $CF_2=CH-C(CH_3)=CH_2$

Recipe: Mutual, 24 hours, 50°C.
Molar Ratio Charged: 50/50

Run No.	Comonomer (X)	% Conversion	Moles $CF_2=CH-C(CH_3)=CH_2$/X Combined	Appearance
1139	$\overline{CF_2-CF=CF-CF_2}$	40	93/7	soft, snappy rubber
1140	$(CH_3)_2C=CH_2$	48	85/15	soft, fairly slow rubber
1141	$CH_2=CHCl$	56	91/9	soft, snappy rubber
1142	$C_6H_5-CH=CH_2$	5	34/66	hard solid
1143	$CF_3-CF=CF_2$	69	98/2	soft, fast rubber
1145	$CH_2=CH-CO_2-C_4H_9$ (n)	92	68/32	short, tough rubber
1144	$CH_2=CH-CN$	74	63/37	soft, snappy rubber
1146	$CF_3-C\equiv C-CF_3$	2	90/10	soft, slow rubber
1147	$CH_2=CFCl$	0	--	-----
1148	cis $CF_3-CH=CH-CF_3$	46	100/0	soft, fairly fast rubber
1149	trans $CF_3-CH=CH-CF_3$	49	100/0	soft, fast rubber
1150	$CH_3-C(CF_3)=CH_2$	32	88/12	soft, fast rubber
1153	$CF_3-CCl=CF_2$	42	100/0	tough, elastic rubber
1152	$CF_2=CFBr$	6	95/5	soft, slow rubber
1154	$CH_3-C(CF_3)=CH-COOH$	8	--	soft rubber
1155	$CH_2=CH-CO-NH_2$	42	100/0	soft, snappy rubber
1156	$CF_3-CH=CH_2$	40	99/1	snappy, fast rubber
1157	$CF_3-CCl=CCl_2$	32	99/1	soft, snappy rubber
1158	$CF_3-CCl=CH_2$	2	81/19	soft, fairly fast rubber
1160	$CF_3-CH=CF_2$	45	99/1	soft, slow rubber

TABLE II
(Continued)

Run No.	Comonomer	% Conversion	Moles $CF_2=CH-C(CH_3)=CH_2/X$ Combined	Appearance
1004	$CF_2=CFCl$	53	89/11	fast rubber
1005	$CF_2=CF-CF=CF_2$	46	86/14	fast, snappy rubber
1006	$CF_2=CCl_2$	65	88/12	fast, snappy rubber
1007	$CH_2=CCl_2$	5	78/22	soft rubber
1008	$CF_2=CHF$	82	84/16	fast, snappy rubber
1010	$CF_3-CCl=CH_2$	20	84/16	soft, slow rubber
1011	none	104	(found 35.96% F.,) (theor. 36.24%)	tough, fast rubber

Recipe: Cumene Hydroperoxide Redox, 24 hours, 20°C.
Molar Ratio Charged: 50/50

Run No.	Comonomer	% Conversion	Moles Combined	Appearance
1130	$CF_2=CF_2$	53	87/13	soft, sticky, fast rubber

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TABLE III

COPOLYMERS OF CF_3-CH=CH_2 AND CF_3-CCl=CH_2

Recipe: Persulfate-bisulfite-iron suspension, 20°C.
Molar Ratio Charged: 50/50

CF_3-CH=CH_2 Copolymers

Run No.	Comonomer (X)	Mole % Ratio Combined, CF_3-CH=CH_2/X	% Conversion	Hours Polymerization	Appearance
811	CH_2=CFCl	40/60	26	78	partly plastic, partly glassy.
813	CH_2=CHBr	12/88	10	78	powder
814	none	---	trace	78	possibly product soluble.
816	CF_3-C(CH_3)=CH-COOH	---	zero	41	brown, water soluble crystals
817	CF_3-CCl=CF_2	---	zero	41	---
818	CH_2=CH_2	---	1	41	tacky rubber
819	CF_2=CFBr	---	trace	41	powder
820	$(CF_3)_2$=CF_2	---	trace	41	---
821	CF_3-C(CH_3)=CH_2	---	zero	41	---
822	trans CF_3-CH=CH-CF_3	---	trace	41	plastic
823	CF_2=CF_2	---	trace	41	---
824	cis CF_3-CH=CH-CF_3	---	zero	41	---
825	CF_2=CFH	---	trace	41	---
826	CF_3-C≡C-CF_3	---	zero	41	---
827	CF_3CCl=CCl-CF_3	---	zero	41	---
828	CF_2=CFCl	---	trace	41	flaky powder
829	CH_2=CHCl	29/71	56	41	pliable solid
830	CF_3-CF=CF_2	---	zero	41	---
831	CH_2=CCl_2	5/95	32	41	chalky powder
832	CF_2=CCl	---	trace	41	---

TABLE III
(Continued)

Run No.	Comonomer (X)	Mole % Ratio Combined, CF_3-CH=CH_2/X	% Conversion	Hours Polymerization	Appearance
833	CF_2=CFCl=CF_2	---	trace	41	possibly water soluble
834	CH_2=CF_2	---	trace	41	---
835	CF_2-CF-CF-CF_2	---	trace	--	---
836	CH_2-CH-CN	0/100	35	41	powder
837	CH_2=CH-CO_2-C_4H_9 (n)	13/87	49	41	tacky rubber
838	CF_2=CH-CH=CH_2	73/27	40	41	powder

CF_3-CCl=CH_2 Copolymers

Run No.	(Comonomer (X)	Mole % Ratio Combined, CF_3-CCl=CH_2/X	% Conversion	Hours Polymerization	Appearance
1067	CF_2=CFCl	---	trace	24	---
1068	CF_2=CF-CF=CF_2	---	trace	24	---
1069	CF_2=CH_2	---	zero	24	---
1070	CF_2=CF_2	---	zero	24	---
1071	CF_2=CCl_2	---	zero	24	---
1072	none	---	zero	24	---

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TABLE IV

CF_2=CFCl/CF_2=CH_2/X TERPOLYMERS

Recipe: Persulfate-bisulfite-iron suspension, 20°C.

Run No.	Termonomer (X)	Moles Charged	Moles Combined	% Conversion	Hours Polymerization	Appearance
848	CF_3-CF=CF_2	40/40/20	47/50/3	75	24	short rubber
956	CF_3-CF=CF_2	40/40/20	45/52/3	78	16	short rubber
964	CF_3-CF=CF_2	40/40/20	48/39/13	79	14	short rubber
965	CF_3-CF=CF_2	40/40/20	48/39/13	79	14	short rubber
966	CF_3-CF=CF_2	40/40/20	49/38/13	80	14	short rubber
967	CF_3-CF=CF_2	40/40/20	47/40/13	78	14	short rubber
968	CF_3-CF=CF_2	40/40/20	43/57/0	77	14	short rubber
969/1/	CF_3-CF=CF_2	40/40/20	45/55/0	77	14	short rubber
909	CH_2=CFCl	40/40/20	29/23/48	24	2	slow rubber
970	CH_2=CFCl	40/40/20	39/36/25	85	6	short fast rubber
955	CH_2=CFBr	40/40/20	39/38/23	54	16	slow rubber
987	CH_2=CH_2	49.75/49.75/0.5	49/51/trace	44	20	rubber
976	CH_2=CH_2	37.5/37.5/5	52/48/trace	5	20	powder
1190	CF_2=CFH	40/40/20	44/40/16	19	1/2	rubber
1088	CH_2=CFH	60/30/10	53/47/trace	32	1/2	slightly rubbery

/1/ Runs 848, 956, and 964-969 were combined and blended; the blend was assigned run number 1021.

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TABLE V

MISCELLANEOUS EXPLORATORY POLYMERIZATIONS

Recipe: Persulfate-bisulfite-iron suspension at 20°C.
Charge: 50/50 molar

Run No.	Monomers	Molar Ratio Combined in Polymer	% Conversion	Hours Polymerization	Appearance
783	CF_3-CCl=CCl_2/CF_2=CH_2	---	1	24	powder
843	CF_2=CFCl/CF_2=CFBr	51/49	85	24	powder
807	CH_2=CFCl/CF_2=CFBr	55/45	108	78	brittle solid
808	CH_2=CFCl/CF_3-CF=CF_2	92/8	36	78	dead rubber
812	CH_2=CFCl/CH_2=CHBr	35/65	50	78	powder
839	CH_2=CHBr/CF_2=CF_2	83/17	46	41	powder
840	CH_2=CHBr/CF_2=CFCl	75/25	48	41	powder
841	CH_2=CHBr/CF_2=CCl_2	68/32	24	41	powder

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TABLE VI

COPOLYMERS FOR SCREENING

Code	Composition	% Conversion	Mole % Ratio Combined
999	CF_2=CFCl/CF_2=CH_2/CH_2=CFCl	24	56/8/36
970	CF_2=CFCl/CF_2=CH_2/CH_2=CFCl	35	39/36/25
955	CF_2=CFCl/CF_2=CH_2/CF_2=CFBr	54	39/38/23
1012	CF_2=CH-CH=CH_2/CF_2=CFCl	38	85/15
1013	CF_2=CH-CH=CH_2/CF_2=CF-CF=CF_2	43	68/32
1015	CF_2=CH-CH=CH_2/CF_2=CCl_2	43	84/16
1039	CF_2=CH-CH=CH_2/CH_2=CHCl	27	79/21
1040	CF_2=CH-CH=CH_2/CF_3-CH=CH_2	30	76/24
1044	CF_2=CH-CH=CH_2/CF_3-C(CH_3)=CH_2	37	78/22
1046	CF_2=CH-CF=CH_2/CF_2=CFBr	11	92/8
1049	CF_2=CH-CH=CH_2/CF_2=CH-C(CH_3)=CH_2	92	80/20/1/
1090	CF_2=CH-CH=CH_2/CF_3-CCl=CH_2	42	84/16
1129	CF_2=CH-CH=CH_2/CF_2=CF_2	37	85/15
290	CF_2=CF-CF=CF_2/CH_2=CH-CH=CH_2	48	40/60
291	CF_2=CF-CF=CF_2/CH_2=CH-CH=CH_2	82	34/66
515	CF_2=CF-CF=CF_2/CH_2=CH-CH=CH_2	22	29/71
567	CF_2=CF-CF=CF_2/CH_2=CH-CH=CH_2	27	21/79
568	CF_2=CF-CF=CF_2/CH_2=CH-CH=CH_2	27	24/76
522	CF_2=CF_2/CH_2=CH-CH=CH_2	28	19/81
573	CF_2=CF_2/CH_2=CH-CH=CH_2	23	14/86
576	CF_2=CF_2/CH_2=CH-CH=CH_2	16	24/76

TABLE VI

(Continued)

Code	Composition	% Conversion	Mole % Ratio Combined
1139	$CF_2=CH-C(CH_3)=CH_2/CF_2-CF=CF-CF_2$	40	93/7
1141	$CF_2=CH-C(CH_3)=CH_2/CH_2=CHCl$	56	91/9
1145	$CF_2=CH-C(CH_3)=CH_2/CH_2=CH-CO_2-C_4H_9$ (n)	92	68/32/1/
1144	$CF_2=CH-C(CH_3)=CH_2/CH_2=CH-CN$	74	63/37
1150	$CF_2=CH-C(CH_3)=CH_2/CF_3-C(CH_3)=CH_2$	32	88/12
1004	$CF_2=CH-C(CH_3)=CH_2/CF_2=CFCl$	53	89/11
1005	$CF_2=CH-C(CH_3)=CH_2/CF_2=CF-CF=CF_2$	45	86/14
1006	$CF_2=CH-C(CH_3)=CH_2/CF_2=CCl_2$	65	88/12
1008	$CF_2=CH-C(CH_3)=CH_2/CF_2=CFH$	82	84/16/1/
1010	$CF_2=CH-C(CH_3)=CH_2/CF_3-CCl=CH_2$	20	84/16
1011	$CF_2=CH-C(CH_3)=CH_2$/ALONE	104	---
1130	$CF_2=CH-C(CH_3)=CH_2/CF_2=CF_2$	53	87/13
572	$CF_2=CH_2/CF_2=CF_2$	57	35/65
695	$CF_2=CH_2/CF_2=CFBr$	50	55/45

/1/ Analytical results unexplained.

FILE NO.: LAS-84
JMH:LAS 11-25-53

TABLE VII

COMPARISON OF X-300 CURATIVES

QM Compound Code Number	1F78	1F93	1F99	1F100	1F102	1F104	1F104	1F120
X-300 (pilot plant lot J-3396)	100						100	100
X-300 (laboratory prep.)		100						
X-300 (pilot plant lot J-3839)			100	100	100	100		
Zinc Oxide	5	5	5	5		5	5	5
MDI (Du pont)	5							
MDI, 100% (Monsanto)		5						
Curing agent 105-35			5					
Curing agent 180-56				5	5	5	5	
Curing agent 105-52								5
Temp. °F., for Mold Curing	260	260	260	260	260	260	260	260
Time of Mold Cure, min.	60	60	60	60	60	60	60	60
Tensile strength, psi., mold cure	900		475	2000	1450	900	1400	1150
Mold cure + 16 hrs. at 212°F.	1050	580	750	2300		2100	1400	1150
Mold cure + 64 hrs. at 212°F.		1720						
Elongation, %, Mold Cure	470		350	280	410	400	360	430
Mold cure + 16 hrs. at 212°F.	360	345	220	250		420	320	380
Mold cure + 64 hrs. at 212°F.		320						
Stress at 300%, Mold Cure	350		325		825	600	900	500
Mold cure + 16 hrs. at 212°F.	650	380				1050	1200	650
Mold cure + 64 hrs. at 212°F.		1450						
Hardness, Shore "A", 5 sec. Mold Cure	55		58	65		63	60	59
Mold cure + 16 hrs. at 212°F.	56	56	64	71		62	61	56
Mold cure + 64 hrs. at 212°F.		60						

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